ADSORPTION OF METHYLENE BLUE USING ACTIVATED CARBON FROM MIXED OF PALM OIL PRESS FIBRES AND EMPTY FRUIT BUNCH

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ABSTRACT

Nowadays, palm oil industry wastes such as palm oil empty fruit bunch and palm oil press fibre have been sold as source of energy renewable in Malaysia. In the combustion process of palm oil empty fruit bunch and palm oil press fibre will produce carbon. This carbon can be activated to use in waste water treatment and chemical absorber. Methylene blue was use as adsorbate with different concentration. The activated carbons have been produce using chemical activation using potassium hydroxide. It has been carbonize at 250^{o}C for 24 hour with nitrogen flow and the activation process also as carbonize process with temperature 300^{o}C. The equilibrium study using UV-Visible Spectrophotometer is to make calibration curve and to determine the final concentration of the methylene blue solution. From the experiment, the adsorption graph show the 50% additional percentage weight of empty fruit bunch into palm oil press fibres give the high adsorption percentage and from the lagmuir isotherm it also give the high value R2 and it maximum adsorption capacity is 111.111 mg/g. The characterization of the activated carbon produce have been determine using Fourier Transform Infrared Spectroscopy (FTIR), it presence of –OH (hydroxyl), C-H (alkanes and alkyls), C=O (Ketone or Asidcarbosilik), and C-O-C (esters, eter or phenol).From this research, that can conclude the activated carbon is successfully produce and the characterization of the activated carbon also determine using FTIR. The optima condition is at 50% additional percentage weight of empty fruit bunch into palm oil press fibre.

ABSTRAK

Pada masa kini, di Malaysia, sisa buangan industry sawit seperti tandan kosong dan sabut sawit dijual sebagai bahan bakar untuk menjana tenaga. Dalam proses pembakaran tandan kosong dan sabut sawit ini akan menghasilkan karbon. Karbon ini boleh di aktifkan untuk digunakan dalam proses rawatan air dan penjerapan bahan kimia. Methylena biru digunakan sebagai adsorbate dengan kepekatan awal yang berbeza. Procses pengaktifan yang digunakan adalah mengunakan bahan kimia. Ianya dikarbonkan pada suhu 250^{o}C selama 24 jam dengan disalurkan gas nitrogen dan proses menaktifkan adalah seperti proses dikarbonkan dengan suhu 300^{o}C. Pelajaran keseimbangan dibuat menggunakan UV-Visible Spectrophotometer untuk membuat graf penentukuran dan untuk mencari kepekatan akhir larutan methylena biru. Daripada experiment, graf penjerapan menunjukan 50% tambahan peratus berat sabut sawit kedalam sabut sawit memberi keputusan tertinggi bagi peratus penjerapan dan daripada sesuhu langmuir memberi baca tertinggi untuk R2 dan penjeratan kapasiti maksimun iaitu 111.111 mg/g. Pencirian karbon diaktifkan yang dihasilkan telah ditentukan menggunakan Fourier Transform Infrared Spectroscopy (FTIR), kehadiran –OH (hidroksil0, CH (alkana dan alkyls) dan COC (ester, eter atau fenol). Dari penyelidikan ini, boleh disimpulakan kabon diaktifkan berjaya dihasilkan dan pencirian juga dapat diketahui menggunakan FTIR. Keadaan optima adalah pada berat peratus 50% tambahan tandan kosong kedalam sabut sawit.

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Co	Initial Concentarion of Methylene Blue (mg/L)
Ce	Final Concentration of Methylene Blue (mg/L)
qe	Amount adsorbed at equilibrium in (mg/g)
Qo	Maximum Adsorption Capacity (mg/g)
qm	maximum monolayer adsorption capacity (mg.g)
kL	Adsorption equilibrium constant in (L/mg)

CHAPTER 1

INTRODUCTION

1.1 Research Background

Activated carbon (AC) is the carbonaceous material which an important thing in adsorption process. Its specialty to remove organic and inorganic chemical in waste, odor, taste and colour from any kind of chemical basically in waste water and water treatment based on their amazing properties. Activated carbon has high degree of surface reactivity which can influence its interaction with polar or nonpolar adsorbates. Besides, it also has higher surface area and micro porous structure. Activated carbon are widely use in wastewater treatment to remove harmful chemicals and heavy metal, industrial waste water or industrial flue gas. Their application in industry includes removing organic and inorganic pollutants from drinking water, industrial wastewater treatment, decolorizing of syrups and purification of air and pharmaceutical products.

The demand of the activated carbon is increasing year by year, because, it wide usage in industry. Commercial activated carbon is quite expensive. As such industry now seeks for the cheapest activated carbon derive from agriculture waste or residuals. The residuals can be rice husk, palm oil mill sludge, sawdust or other carbonaceous material. The raw material were processed and optimized to obtain excellent adsorptive properties. Activated carbon can be produced either by chemical or physical activation. Chemical activation only involves single step in heating process to activate the carbon. This process needs chemical activating agent like as $ZnCl_2$, KOH, H_3PO_4 or H_2SO_4 to enhance carbon yield and produce micro pores on the surface of the carbon. Physical activation involves two steps of heating process and does not involve any chemicals.

Dyes (for example a methylene blue) have long and usually been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Colour stuff discharged from these industries will give certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and also difficult to biodegrade.(Yamin *et al*,2007) Many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities

Hence, activated carbon is a suitable absorber material in removal dry in waste water from industry with its ability in absorption and it has high surface area. Activated carbon from palm press fibre and empty fruit bunch of palm oil residue can be obtain from industry that using this residue as combustion material for renewable energy.

1.2 Problem Statement

Industrial processing of palm oil from fresh palm oil fruit will produce biomass waste. Among of them is empty fruit brunch (EFB), palm pressed fibres (PPF), palm kernel cake and many more. At this time, this biomass waste only using as fuel in palm oil processing industry. A lot of biomass waste not being utilizes and converted to high valued product such as renewable energy. This combustion process will produce a lot of carbon solid and it only remains in the furnace than consider as waste.

1.3 Objective of Study

At the end of this study, it is necessary:

1. To produce and characterized the activated carbon from the palm press fibre with different additional empty fruit bunch using chemical activation process.
2. To study the optimal condition (additional composition empty fruit bunch into palm press fibre) of absorption process.
3. To study the effect of concentration of the methylene blue (MB) solution to the adsorption capacity.
4. To utilized the use of carbon produce from carbonization of palm oil residue that can be reuse or recycle to be another valuable product.

1.4 Research Scope

The scope of this study consists of:

1. Preparation of activated carbon using KOH as chemical activation
2. The initial concentration of methylene blue from 50, 100, 200, 300 and 400 mg/L
3. For methylene blue analysis, by using UV-Visible Spectrophotometer, the wavelength use is 665nm.
4. The effect of different percentage additional EFB into absorption process.
5. Activated carbon produce characterization using Fourier Transform Infrared Spectroscopy (FTIR)

1.5 Rationale and Significance of Study

Oil palm shredded pressed fibres and palm oil empty fruit bunch has been using in oil palm industry source of energy as fuel and it will cause air pollution. After the burning process the fiber will change into carbon and it will be as waste. That carbon can be use again as activated carbon for another process such as waste water treatment and chemical absorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Activated Carbon

Activated carbon (AC) is the carbonaceous material which an important thing in adsorption process. Its specialty to remove organic and inorganic chemical in waste, odor, taste and colour from any kind of chemical basically in waste water and water treatment based on their amazing properties. Activated carbon has high degree of surface reactivity which can influence its interaction with polar or nonpolar adsorbates. Besides, it also has higher surface area and micro porous structure. Activated carbon are widely use in wastewater treatment to remove harmful chemicals and heavy metal, industrial waste water or industrial flue gas. Their application in industry includes removing organic and inorganic pollutants from drinking water, industrial wastewater treatment, decolorizing of syrups and purification of air and pharmaceutical products. Activated carbon properties depend on:

i. The polarity of the surface.
ii. Pore size distribution.
iii. The carbon surface area.
iv. Chemical and porous structure of carbon
v. Physical and chemical characteristic of adsorbate. (Bansal, 2005)
vi. Heating method. (Foo *et al*, 2011)

2.2 Application of activated Carbon

Activated carbon is widely used in industrial waste water and many more. The examples of its usage are:

i. Decolorizing of syrups, dye, sugars and molasses
ii. Removal of Nitrogen from air.
iii. Removal of SO_X and NOx
iv. Recovery of solvent vapors.
v. Purification of helium
vi. Water purification in removing in wastewater industry
vii. Purification many chemical, pharmaceutical product and food industry
viii. Air purification in inhabited space to remove odor.

2.3 Activated Carbon from Agriculture Waste Based

Activated carbon can be produce from organic material such as risk husk, coconut fiber and etc, also can find another new use for this activated carbon and the different method in journal.. "Liquid and solid waste, are a huge and always increasing problem for the industries and the environment. One of the most popular ways of dealing with solid waste is its use as a raw material for the production of activated carbons that can be subsequently employed for the removal of pollutants from liquid waste. As adsorbents, activated carbons bear extremely large surface area, with varying porous structure consisting of a network of interconnected macropores, mesopores and micropores. Their surface area also presents great diversity in terms of surface charge and surface groups, depending on the original raw material and the way of activation. For a raw material to be used for activated carbon production, it should have high carbon content. Agricultural waste is commonly exploited this way (Michailof *et al*, 2008)." Nowadays, this agriculture waste will be selling as material for combustion of furnace or boiler in industrial.

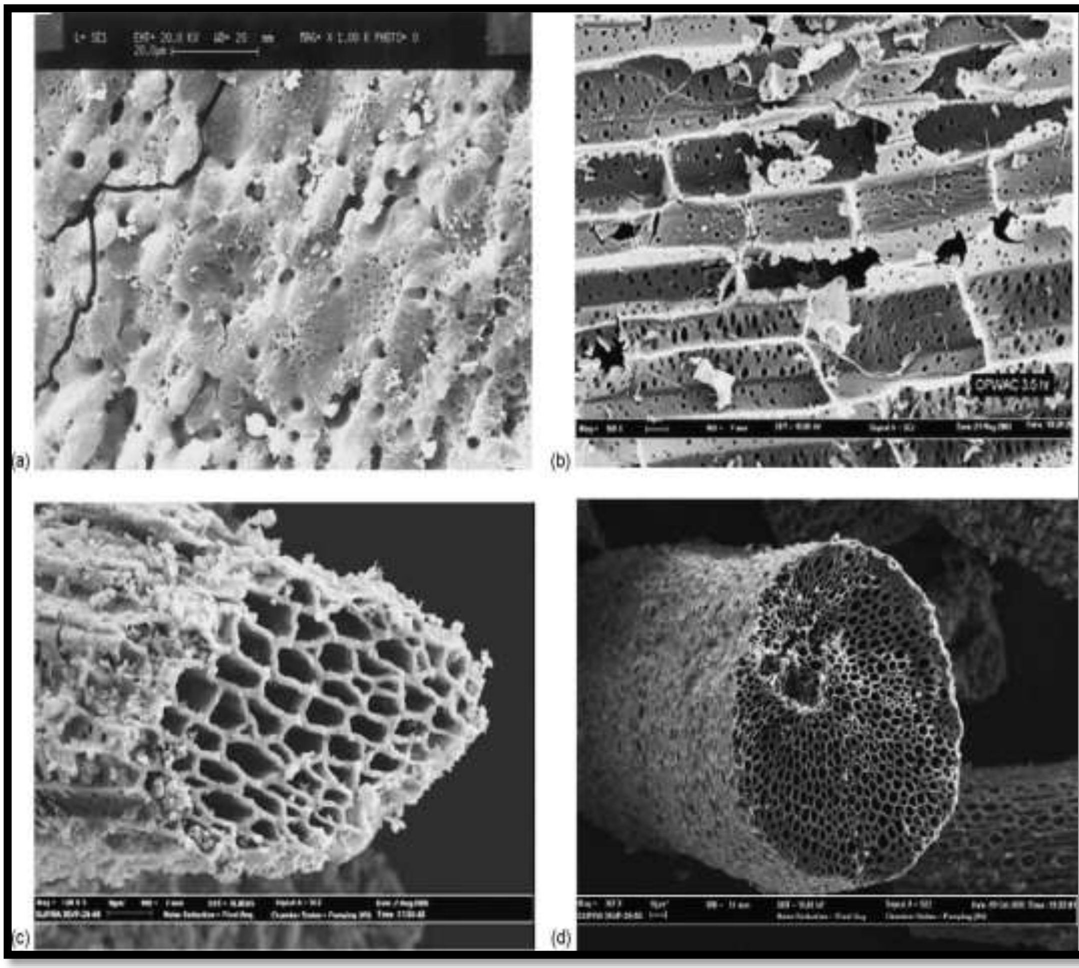

Figure 2.1: Scanning electron micrographs (SEM) of the activated carbons prepared from raw palm stone (a), oil palm wood (b), oil palm shell (c) and oil palm fiber (d)

Sources: Foo *et al*, (2009)

2.4 Preparation of Activated Carbon

For preparation of activated carbon, the material needs to be carbonizing at the high temperature without oxygen or with hydrogen flow to produce the carbon. The activation process can be doing before or after carbonizing process, it depends to the method that used. To activate the carbon there have to activation process, physical activation process and chemical activation process.

2.4.1 Physical Activation Process

For the physical process, the activate process will be made before the carbonizing process. The material will be boiling in distilled water at 150^{o}C for 2 hour, than will be dehydrate in oven to remove moisture. Than the material will be carbonize to produce activated carbon. (Alam *et al*, 2007)

2.4.2 Chemical Activation Process

For the chemical process, the char produce can be activated by using chemical such as KOH, ZnCl2, H3PO4 or H2SO4 to enhance carbon yield and produce micro pores on the surface of the carbon. The carbon can be active before or after carbonize. By using KOH as agent to make the activation. The char produce will be soak in KOH solution with an impregnation (char: KOH) ratio (wt.%). (Foo *et al*, 2011). Than the soaked char will be dehydrate in oven to remove moisture and will be carbonize again with high temperature.

2.5 Palm Oil Biomass as Source Renewable Energy

The demand of energy sources and depleting supply of natural sources such as crude oil and natural gas will led to higher government expenditures subsidies to keep retail fuel price. So, another alternative to replace the energy sources such as fuel, the new thing have been discover that it use the agriculture waste as renewable energy source. Biomass power plant has been build to generate electricity energy, combustion agent for boiler and furnace for industrial and many more. (Mohammed *et al*, 2011). Recycling of palm oil waste as resources for activated carbons production are ready mention at the above. Oil palm waste as the energy sources for power generation to generate heat and electricity by combustion. The used of palm oil waste as activated carbon has been discovered and it real give excellent absorption. (Foo et al, 2009)

2.5.1 Palm Oil Press Fibres (PPF)

In Malaysia, biomass mass waste such as wood waste, agricultural crop, mill residues and many more give approximately 15 million tones collected/year.(FRIM 2010). A palm-pressed fibre has been category as mill residues in oil palm process. Oil palm press fibre (OPPF) or mesocarp fibre, is the fibre obtained after expressing oil from the fruit mesocarp. On average, for every tonne of fresh fruit bunches (FFB) processed, 120 kg mesocarp fibre was produced. In 1993, an estimated 4.74 million tonnes of FFB was produced. (Astimar *et al*., 2002) In this time, palm pressed fibres usually using as fuel in oil palm process plant. From the Figure 2.2 palm pressed fibres come from plam fruit, after extraction process palm fruit will be dry and it called palm pressed fibres.

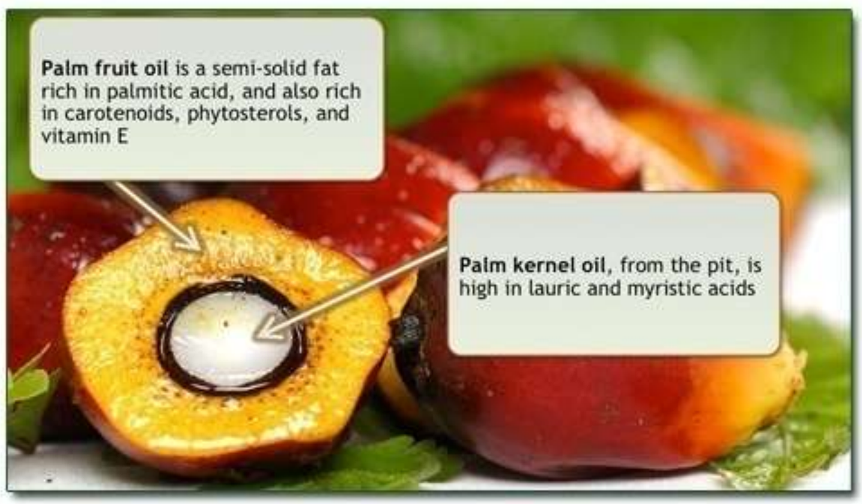

Figure 2.2: Cross Section of Palm Oil Fruit

2.5.2 Composition of Palm Oil Pressed Fibres (PPF)

Mostly characteristic of these residues is lignifications of the cellulose fibres, hemicelluloses, lignin and ash contain. Chemicals test has been made by using chemical treatment such as NaOH, KOH and many more to remove the unused contain. Table 2.1 shows the chemical composition of untreated palm-press fibres. It contain 39.9% of cellulose, 28.9% of hemicelluloses, 20.3 % of lignin and 3.6% ash contain. Table 2.2 show the effect of chemical pretreatment on the compositon of palm-press fibre. (Tong and Hamzah., 1989)

Table 2.1: Chemical Composition of Untreated Palm-Press Fibres

% Of Dry Matter				
	Cellulose	Hemicellulose	Lignin	Ash
Untreated	39.9	28.9	20.3	3.6

Source: Tong (1989)

Table 2.2: Effect of Chemical Pretreatment on the Composition of Palm-Press Fibres

% Of Dry Matter				
	Cellulose	Hemicellulose	Lignin	Ash
NaOH	40.7	29.1	8.0	9.2
KOH	44.5	27.7	14.6	3.3
$Ca(OH)_2$	36.9	30.1	12.4	4.4
Na_2CO_3	38.1	27.5	10.2	4.9
NH3	36.5	31.9	11.9	3.4
$CO(NH_2)_2$	36.4	35.5	15.9	9.8

Source: Tong (1989)

2.5.3 Palm Oil Empty Fruit Bunch (EFB)

Oil palms fruit will be harvested usually after 3 years from planting, but maximum yield can be achieved in the 12–14th year, and then continuously declines until the end of the 5th year. The Malaysian palm oil industry has grown tremendously over the last 25 years to become a very important agriculture-based industry, where the country is today the world's leading producer and exporter of palm oil. The palm oil production has increased from 2.5 million tonnes in 1980 to 17.8 million tonnes in 2009 and presently Malaysia's production for 47% of the palm oil world production. "Palm oil forms about 10% of the whole palm oil tree, while the other 90% remains biomass. For example, fresh fruit bunch contains only 21% palm oil, while the rest 14–15% fiber, 6–7% palm kernel, 6–7% shell and 23% empty fruit bunch (EFB) are left as biomass" (Mohammed *et al*, 2011).

Figure 2.3: Palm Oil Empty Fruit Bunch

Source: Mohammed *et al*, (2011)

2.5.4 Composition of Empty Fruit Bunch (EFB)

Table 2.3 show the chemical compostion of palm oil empaty fruit bunch, it contain 38.3% of cellulose, 35.3% of hemicelluloses, 22.1% of lignin and 1.6 ash contain. Basically, the component has been build from the C-O that can help in production of carbon.

Table 2.3: Chemical Composition of Palm Oil Empty Fruit Bunch

Component	Chemical Composition (wt)%
Cellulose	38.3
Hemicellulose	35.3
Lignin	22.1
Ash	1.6

Source: Mohammed *et al*, (2011)

2.6 Introduction of Methylene Blue

Also called as dye, methylene blue (MB), it slassification Number is 52,015, with chemical formula=$C_{16}H_{18}N_3ClS$,. It molecule weight is 319.85 g/mol, the maximum wave length is 668 nm (measured value). Methylene blue usually use in absorption study to measure the absortion of the activated carbon. It also harmfully and shout be hander safely. Make sure do not this chemical with bear hand.

2.6.1 Characteristic of Methylene Blue

The characteristic of methylene blue are summarizing in Table 2.4 below.

Table 2.4: Characteristic of Methylene Blue

IUPAC name	
Other names	Dye
Molecular formula	$C_{16}H_{18}N_3SCl$
Molar mass (g/mol)	319.85
Appearance	Dark green powder Blue solution when dissolved in water
Density (g/cm^3)	1.757 (22^{o}C)

Melting point (^{o}C)	190
Solubility in water	50 g/L ($20^{o}C$)
Acidity (pKa)	3.8

2.7 Langmuir Isotherm

Langmuir isotherm is a semi-empirical isotherm derived from a proposed kinetic mechanism. Langmuir isotherm is a model for monolayer localized physical adsorption on homogeneous surface; may be extended with heterogeneity effects, lateral interactions and multilayer effects. It is based on four assumptions:

i. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
ii. Adsorbed molecules do not interact.
iii. All adsorption occurs through the same mechanism.
iv. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. (Ignatowicz, 2011)

The Langmuir equation may be written as:

$$qe = qm\frac{kL}{1+kL} \qquad (2.1)$$

Where,

qe (mg/g) = amount of methylene blue adsorbed on the adsorbent surface at equilibrium,

c (mg/L) = methylene blue concentration in aqueous solutions at equilibrium,

qm (mg/g) = maximum monolayer adsorption capacity,

kL = constant related to the free energy of adsorption.

Equation 2.1 can be linaerized to form equation 2.2 at the below.